Residual Gas Analysis (RGA) and Shear Strength Characteristics of a Silver-Filled Epoxy and Polyimide Under Long-Term, High-Temperature Storage Conditions

Kansas City Division

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**RESIDUAL GAS ANALYSIS (RGA) AND SHEAR STRENGTH
CHARACTERISTICS OF A SILVER-FILLED EPOXY AND POLYIMIDE
UNDER LONG-TERM, HIGH-TEMPERATURE STORAGE CONDITIONS**

B. E. Adams

Published April 1994

Final Report

B. E. Adams, Project Leader

**Technical Communications
Kansas City Division**

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A E R O S P A C E

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Abstract

Long-term aging characteristics for a silver-filled epoxy and a silver-filled polyimide were investigated. Leadless chip carriers (LCCs) containing die attached with epoxy or polyimide were aged at 25°C, 100°C, 150°C, and 200°C for up to six months. Residual gas analysis (RGA) and die shear testing were performed on each package. Results indicate that the epoxy can withstand storage at 150°C with no increase in internal moisture. The polyimide could only be stored at 100°C. No loss in shear strength for epoxy or polyimide was noted at any storage condition.

Summary

Introduction of organic materials into hermetically sealed electronic packages increases the risk of failure due to contamination. The contaminants of concern are moisture and ionics. This combination can lead to unwanted electrical pathways and/or corrosion. To minimize sealed-in moisture, packages are vacuum-baked for 16 hours at 200°C and Au/Sn solder-sealed in a glove box purged with dry nitrogen. Even following this procedure, the package plating and organic adhesive can still outgas moisture during high-temperature storage.

The purpose of this investigation was to determine the long-term, high-temperature storage ability of a silver-filled epoxy and a silver-filled polyimide. The adhesives were to be used for die attach into 20-pin leadless chip carrier (LCC) packages, hermetically sealed in dry nitrogen, and residual gas analyzed (RGA) after long-term storage at 25°C, 100°C, 150°C, and 200°C. Die shear testing was also to be performed to measure mechanical degradation.

Before running a long-term aging experiment, the optimum cure was determined for each material. An array of cure times and temperatures was run for each material, and shear test and RGA results were compared. The most favorable combination of results was used as the optimum cure cycle. Differential scanning calorimetry (DSC) was also run on the epoxy to verify that the cure cycle selected resulted in 100% cure of the material. The cure schedules chosen were 175°C, 105 minutes for the epoxy and 225°C, 180 minutes for the polyimide.

Four aging temperatures were selected for the long-term storage experiment: 25°C, 100°C, 150°C, and 200°C. These temperatures were selected to cover the upper range of environmental testing temperatures for electronics as required by military specification 883C. Samples of three epoxy packages, three polyimide packages, and one empty control package were pulled from each aging temperature and tested after 1, 2, 7, 14, 30, 60, 120, and 180 days of aging. All RGA was done by Oneida, and the shear testing was done at the Kansas City Division (KCD) in

Semiconductor Package Assembly,
Department 78.

The overall results indicated that silver-filled epoxy can be stored up to 150°C with no increase in the moisture content within the package. After seven days of aging at 200°C, a great increase in moisture occurred, peaking at 15%, indicating thermal degradation of the material. However, shear test data indicated that the thermal breakdown was not significant enough to lose mechanical integrity. For the polyimide, storage as low as 150°C caused a large amount of moisture to be outgassed. Again, the material was not degraded mechanically as indicated by the shear strength.

Currently the military specification requires the moisture content within an hermetically sealed package to be less than 3000 ppmv for class S material and 5000 ppmv for class B material. Based on the results of the aging test, the epoxy can safely withstand thermal aging of 150°C for long durations but not 200°C for more than 72 hours. The polyimide should not be exposed to more than 100°C if a similar curing cycle is used.

Discussion

Scope and Purpose

The purpose of this investigation was to determine the long-term, high-temperature storage ability of a silver-filled epoxy and a silver-filled polyimide. The adhesives were to be used for die attach into 20-pin leadless chip carrier (LCC) packages, hermetically sealed in dry nitrogen, and residual gas analyzed (RGA) after long-term storage at 25°C, 100°C, 150°C, and 200°C. Die shear testing was also to be performed to measure mechanical degradation.

Activity

Introduction

The atmosphere within an hermetic microelectronic package has direct impact on the electrical functioning and useful lifetime of the devices inside. The introduction of an organic material into an hermetically sealed electronic package increases the risk of failure due to contamination. Contaminants from organics which may induce or accelerate electrical failures are ionized elements and outgassing of moisture. The outgassing of moisture is feared because during temperature cycling moisture in the package can condense and extract ionic contamination from the adhesive. The water then becomes a medium for ionic migration. This can create unwanted electrical paths and potential for corrosion. The contamination can attack the wire bond, die interface, or the integrated circuit (IC) itself. The ionic contaminants feared most are chloride (Cl^-), hydronium (H^+),

sodium (Na^+), and potassium (K^+). These contaminants can corrode aluminum or diffuse through silicon oxide, polysilicon, and aluminum; congregate in the gate area of an IC; and cause a change in the threshold voltage.

At AlliedSignal Inc., Kansas City Division (KCD), hybrids are fluxless solder-sealed in a glove box containing a nitrogen atmosphere. The dew point of the nitrogen-purged glove box is held at -75°C, relating to approximately 1.0 ppmv water. Prior to sealing, the parts are vacuum baked for 16 hours at 150°C and 1000 micrometers. The purpose of the bake is to drive off moisture absorbed from the atmosphere by the package and adhesive during the hybrid fabrication. Furthermore, leak testing is done to ensure that the solder seal is hermetic. The hybrid is considered sealed if the leak rate of helium is $5 \times 10^{-8} \text{ cm}^3/\text{min}$ or less. But even following this procedure, typical values of moisture in hermetic packages range from 500 ppm to 3000 ppm. Internal hydrocarbon volumes run in the 0 to 1000 ppm range and carbon dioxide in the 1500 to 20000 ppm range. The sources of these contaminating gases are the package plating and organic adhesives used for die and substrate attachment.

Experimental Approach

Cure Optimization

Before running a long-term outgassing experiment of organic material, testing must be run to determine the optimum cure cycle for the adhesives. Outgassing of organic material sealed in a package is

directly proportional to its cure. An undercured adhesive will outgas more moisture than fully cured resins because the curing mechanism is basically a condensation reaction. Furthermore, solvent carriers may not be totally burned off, increasing the quantity of contaminating vapors within the package. However, extending the cure time is not detrimental.

Two experiments were run to determine the optimum cure cycle for the polyimide and epoxy. First, arrays of curing times and temperatures were picked based on the manufacturers' recommendations. Three different temperatures and three different times were selected to cure the epoxy and polyimide. For the epoxy the cure temperatures were 150°C, 175°C, and 200°C. The cure times were 30 minutes, 105 minutes, and 180 minutes. For the polyimide the cure temperatures were 150°C, 225°C, and 300°C at times of 30 minutes, 105 minutes, and 180 minutes. Samples of five parts were cured at the high and low temperatures for the high and low times. Also, five parts were cured at the middle time and temperature. The samples were then lidded, leak tested, and aged at 168°C for 10 hours followed by 137°C for 62 hours. All parts were then sent to Oneida for residual gas analysis (RGA). Upon return, each sample was delidded and shear tested.

The differential scanning calorimeter (DSC) was the second tool used to determine full cure of an epoxy system. The DSC measures the heat of reaction and the reaction temperature during the curing of the epoxy. The reaction rate is directly proportional to the rate of heat generation, providing the cure reaction is the only thermal event. The DSC signal is proportional to the rate of cure, and the total area under the exothermic peak represents the heat of reaction. Taken together, these allow the characterization

of the rate of cure and extent of reaction under a variety of processing conditions. Dynamic DSC, where the adhesive is cured during a linear temperature ramp, is most useful for obtaining the total heat of reaction and evaluating the temperature dependence of the cure. During this investigation, dynamic DSC scans were made at heating rates of 2.5, 5, 10, and 20°C/min.

The activation energy of the reaction can also be determined from these experiments. It has been observed that the peak exotherm temperature (T_p) varies in a predictable manner with the heating rate, and the extent of reaction at the peak exotherm is constant and independent of heating rate. Plotting $\ln$ (heating rate) versus $1/T$, where T is the exotherm peak absolute temperature, yields a straight line whose slope is equal to $-E/R$ where R is the gas constant and E is the activation energy.

Long-Term Storage

With the optimum cure cycle determined, a long-term aging test could be run to observe the effect of temperature and time on the sealed packages. Four aging temperatures were selected for the experiment. These were 25°C, 100°C, 150°C, and 200°C. These temperatures were chosen to cover the upper range of temperatures used for environmental testing of electronic components as required in military specification 883C. The parts were placed in ovens at each of these temperatures and samples were pulled out after 1 day, 2 days, 7 days, 14 days, 30 days, 60 days, 120 days, and 180 days of aging. A total of seven parts was pulled at each test day for each test temperature. Three packages contained epoxy, three contained polyimide, and one was a control (empty). A total of 224 packages was tested. The parts were sent

to Oneida for RGA, then returned for die shear testing.

A flow chart of the packaging process is shown in Figure 1. (All figures appear following the text.) Marking, die attach, and curing were all accomplished in one day. Curing was done in a convection oven with a room air atmosphere. On the second day all parts were cleaned by vapor degreasing in trichlorotrifluoroethane, then vacuum-baked at 200°C for 16 hours at 150-micron vacuum. The vacuum oven also acts as a lock way entrance into the RICO sealer which is run in a strictly controlled nitrogen atmosphere (dew point -75°C). All parts were fluxless solder sealed with 80-20 Au/Sn solder in the RICO sealer on the third day. Leak testing on the following day revealed 22 parts which did not pass the 5×10^{-8} cm³/min maximum leak rate. Replacement parts were assembled and the aging test began two weeks after the beginning of the assembly of the first 224 parts.

Accomplishments

The results in Tables 1 through 10 of the RGA and shear tests which were run to determine optimum cure cycle indicated that the optimum cure for the epoxy was 175°C for 105 minutes. (All tables appear following the text.) For the polyimide, 225°C at 150 minutes was the cure selected as best. These were picked based on the combination of highest shear strength with lowest outgassing characteristics. Although the shear strength was highest at 150°C for the polyimide, the outgassing results were too high. Since the shear strength of all samples cured at 300°C did not meet the mil-spec 883C requirements, the 225°C cure schedule was selected. The cure time was increased to further dry the adhesive to reduce the outgassing quantity.

Results of the DSC experiments can be seen in Figures 2 through 6. From Figure 5 it can be seen that full cure of the epoxy takes place in six minutes when cured at 175°C. However, based on the earlier experiment, the cure time was maintained at 105 minutes. Figure 6 was plotted using the peak exothermic temperatures and heating rates used in the DSC experiments shown in Figures 2 through 4. The slope of the line represents the activation energy of the curing reaction.

Results of the aging test at multiple temperatures can be seen in Figures 7 through 12. The shear strength data shown in Figures 7 and 8 indicate that aging temperatures up to 200°C have no effect on the adhesive strength. The variation of strengths for a given aging temperature is an indication of the assemblers' ability to use a consistent amount of adhesive per die. All dice were manually attached, and application of the adhesive was done by hand using a microknife or toothpick.

The moisture content of the empty packages shown in Figure 9 indicates a minimum level that can be attained using this sealing process. That minimum quantity of moisture ranges between 800 and 4500 ppmv. The RGA results shown in Figures 10 through 13 indicate that aging packages containing polyimide or epoxy at 25°C or 100°C had no impact on the water content. The quantity of moisture fell within the range of the empty control packages. However, at 150°C significant amounts of water outgassed by the polyimide after 1440 hours of aging as shown in Figure 14. By contrast, the epoxy moisture content continued to remain low at 150°C aging as shown in Figure 15. Figure 16 shows at 200°C aging the water content for polyimide peaked at 16%. Further investigation into the excess water outgassed by the polyimide at 150°C

suggested that the material was not fully cured. Sandia National Laboratories/New Mexico suggests a top curing temperature of 300°C to 350°C for the polyimide to fully cure the material. However, the data from the first experiment showed the minimum shear strength could not be met using that curing temperature.

For the epoxy, aging up to and including 150°C showed no increase in the water content within the sealed package. However, as shown in Figure 17, after aging for seven days at 200°C a great increase in water content occurred, peaking at 15% after four months. Since total cure was ensured by DSC, thermal decomposition of the epoxy must be taking place at 200°C. Although thermal degradation is taking place, it still has not reached a point where the physical strength has been affected. As mentioned earlier, Figure 8 shows no loss of shear strength of the epoxy at any aging temperature.

Currently the military specification requires the moisture content within an hermetically sealed package to be less than 3000 ppmv for class S material and 5000 ppmv for class B material. From the results of the aging test, the epoxy can safely withstand thermal aging of 150°C for long durations, but not 200°C for more than 72 hours. The polyimide should not be exposed to more than 100°C if a similar curing cycle is used.

Figure 1. Process Flow for Adhesive Die Attach

Figure 2. Results of First Dynamic DSC Experiment

Figure 3. Results of Second Dynamic DSC Experiment

Figure 4. Results of Third Dynamic DSC Experiment

Figure 5. Cure Rate of Epoxy at Various Temperatures

Figure 6. Activation Energy for Curing Reaction of Epoxy

Figure 7. Die Shear Strength of Polyimide Aged at Various Temperatures

Figure 8. Die Shear Strength of Epoxy Aged at Various Temperatures

Figure 9. Moisture Content of Empty Control Packages for Each Aging Temperature

Figure 10. Moisture Content of Packages Containing Polyimide Aged at 25°C

Figure 11. Moisture Content of Packages Containing Epoxy Aged at 25°C

Figure 12. Moisture Content of Packages Containing Polyimide Aged at 100°C

Figure 13. Moisture Content of Packages Containing Epoxy Aged at 100°C

Figure 14. Moisture Content of Packages Containing Polyimide Aged at 150°C

Figure 15. Moisture Content of Packages Containing Epoxy Aged at 150°C

Figure 16. Moisture Content of Packages Containing Polyimide Aged at 200°C

Figure 17. Moisture Content of Packages Containing Epoxy Aged at 200°C

Table 1. Shear Strength and RGA Results for Polyimide Cured at 150°C for 30 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	8.70	99.1	1363	1545	5992	449
2	6.70	98.9	1043	1640	7367	490
3	10.0	98.2	2388	8723	6012	614
4	5.85	99.1	1564	2080	5281	435
5	6.30	98.7	2336	4868	4626	753
Average	7.51	98.8	1739	3771	5856	548

*SS = Shear Strength

**HC = Hydrocarbon

Table 2. Shear Strength and RGA Results for Polyimide Cured at 150°C for 180 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	8.25	98.4	2481	4030	8242	792
2	8.85	98.9	1784	4392	4799	620
3	7.20	98.4	3031	5107	7241	710
4	8.90	98.9	1464	3849	5459	346
5	6.80	99.1	1031	2422	4816	349
Average	8.00	98.7	1958	3960	6111	563

*SS = Shear Strength

**HC = Hydrocarbon

Table 3. Shear Strength and RGA Results for Polyimide Cured at 300°C for 30 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	2.65	99.5	640	1768	2243	ND
2	2.30	99.5	802	1613	2235	ND
3	1.80	99.5	570	1477	3047	ND
4	2.15	99.6	674	1527	2186	ND
5	5.25	99.4	713	1547	3497	ND
Average	2.83	99.5	680	1590	2642	ND

*SS = Shear Strength

**HC = Hydrocarbon

Table 4. Shear Strength and RGA Results for Polyimide Cured at 300°C for 180 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	1.85	99.6	551	1652	1707	100
2	1.85	99.5	784	2197	1475	113
3	2.70	99.6	563	1366	1679	113
4	2.75	99.7	528	1605	899	100
5	1.90	99.7	455	1248	1437	100
Average	2.21	99.6	576	1614	1439	105

*SS = Shear Strength

**HC = Hydrocarbon

Table 5. Shear Strength and RGA Results for Polyimide Cured at 225°C for 105 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	5.00	99.4	773	1074	4466	167
2	4.60	99.0	2787	2390	4187	444
3	3.00	99.3	673	790	5196	193
4	5.80	99.3	852	1275	4865	212
5	3.45	99.4	799	1172	3619	169
Average	4.37	99.3	1177	1340	4467	237

*SS = Shear Strength

**HC = Hydrocarbon

Table 6. Shear Strength and RGA Results for Epoxy Cured at 175°C for 105 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	10.0	99.4	1409	1846	2822	282
2	9.50	99.5	860	1063	3056	203
3	10.0	99.3	987	1375	4483	166
4	10.0	99.1	3202	3146	2329	385
5	8.65	99.4	889	1205	3491	180
Average	9.63	99.4	1469	1727	3236	243

*SS = Shear Strength

**HC = Hydrocarbon

Table 7. Shear Strength and RGA Results for Epoxy Cured at 150°C for 30 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	6.70	98.8	1310	2957	7158	259
2	4.85	99.4	1024	1322	3202	202
3	5.00	99.4	785	1144	3840	231
4	6.65	99.2	1797	2248	4161	275
5	5.85	99.3	1028	1601	4010	245
Average	5.81	99.2	1189	1854	4474	242

*SS = Shear Strength

**HC = Hydrocarbon

Table 8. Shear Strength and RGA Results for Epoxy Cured at 150°C for 180 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	10.0	99.3	1008	1084	4060	154
2	6.50	99.4	693	995	3750	152
3	8.60	99.5	667	586	3532	111
4	7.85	99.5	599	741	3242	134
5	---	99.4	930	1363	3548	195
Average	8.24	99.4	779	954	3626	149

*SS = Shear Strength

**HC = Hydrocarbon

Table 9. Shear Strength and RGA Results for Epoxy Cured at 200°C for 30 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	4.70	99.1	1867	2530	4036	287
2	8.55	99.5	957	1424	2706	170
3	4.50	99.3	861	1029	5379	206
4	10.0	99.1	2015	2871	3860	224
5	---	99.4	669	896	3977	178
Average	6.94	99.3	1274	1750	3992	213

*SS = Shear Strength

**HC = Hydrocarbon

Table 10. Shear Strength and RGA Results for Epoxy Cured at 200°C for 180 Minutes

Sample ID	SS* (kg)	N ₂ (%)	CO ₂ (ppmv)	H ₂ O (ppmv)	H ₂ (ppmv)	HC** (ppmv)
1	8.55	99.3	1219	1332	4573	147
2	7.05	99.5	892	1111	2946	137
3	10.0	99.2	968	1487	5367	139
4	6.25	99.1	2109	2009	4960	221
5	---	---	---	---	---	---
Average	7.96	99.3	1297	1485	4462	161

*SS = Shear Strength

**HC = Hydrocarbon

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